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CR-128585

FINAL REPORT

ADDITIONAL STUDIES FOR THE

SPECTROPHOTOMETRIC MEASUREMENT

OF IODINE IN WATER

Contract NAS 9-12769

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Prepared for:

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Houston, Texas 77058

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ABSTRACT

Previous work in Iodine Spectroscopy is briefly reviewed. Continued studies of the direct spectrophotometric determination of aqueous iodine complexed with potassium iodide show that free iodine is optimally determined at the isosbestic for these solutions. The effects on iodine determinations of turbidity and chemical substances (in trace amounts) is discussed and illustrated. At the levels tested, iodine measurements are not significantly altered by such substances.

The main objective of the present work--a preliminary design for an on-line, automated iodine monitor with eventual capability of operating also as a controller--is analyzed and developed in detail with respect to optics, mechanics, and circuitry. The resulting design features a single beam colorimeter operating at two wavelengths (using a rotating filter wheel). A flow-through sample cell allows the instrument to operate continuously, except for momentary stop flow when measurements are made. The timed automatic cycling of the system may be interrupted whenever desired, for manual operation. An analog output signal permits controlling an iodine generator.

1.0 INTRODUCTION

NASA-MSC has a need for an automated iodine monitoring system which will also function as a control system for an iodine generator/applicator in the potable water system of future spacecraft.

Of the several methods of measuring aqueous iodine, the direct spectrophotometric technique appeared best suited for the spacecraft application. Not only does this approach offer the desired sensitivity, operational convenience, and simple instrumentation, it also lends itself, through appropriate design, to actuating and controlling an iodine generator.*

Having previously demonstrated the feasibility of direct spectrometric determinations of aqueous iodine, Beckman Instruments, Inc. developed a prototype instrument, under Contract NAS 9-11879, for the NASA Manned Spacecraft Center. This instrument, successfully used at MSC, was a portable, battery-powered, specific-for-iodine colorimeter requiring manual operation and a stock solution (pure H_2O) to get a reading.

Because the development program for this instrument was so successful, it appeared feasible to incorporate the basic design into a fully-automated, on-line monitor with eventual capability of serving not only as a monitor but also a controller. The further study of iodine spectroscopy and the development of a preliminary design for such an instrument is the subject of this report.

2.0 IODINE-IODIDE SPECTROSCOPY

Iodine imparts a yellow-brown color to water, even in high dilution. In the visible region, aqueous iodine shows a broad absorption band centered at 460 nm

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*For example, a modification of the unit developed by Life Systems, Inc. (NASA CR-111854, Contract NAS 1-9917).

(Figure 1). If iodide (KI in our work) is also present, a narrower, more pronounced band--representing the tri-iodide absorption--appears at 350 nm in the near ultraviolet (Figure 2). The iodine-iodide complex largely distorts the 460 nm iodine band (low KI levels) or even removes it (higher KI concentrations) as shown in Figure 2. A close inspection of these spectrograms shows that although iodine alone may be measured at 460 nm, its accurate determination in an iodide solution will be subject to appreciable error (depending on the KI level) if measured at this wavelength. However, consider the family of curves converging and crossing at 467 nm (Figure 3). When the iodine concentration changes (two levels shown in Figure 2), this point moves up or down accordingly, but always at the same wavelength! Large variations in the potassium iodide level do not disturb this point where, for a given iodine level, the absorption is constant.

This crossover point (which could occur anywhere) is very close to the iodine maximum absorption wavelength. If it were displaced very much on either side of this maximum, sensitivity would suffer, as clearly illustrated in Figure 4, where the absorbance mode of the DK Spectrophotometer was used to generate the spectrograms.

This crossover phenomenon is identified as the "isosbestic point" (Greek: isos, equal; bestos, extinguished). It occurs when dissolved substances can exist in two or more light absorbing forms in equilibrium. Potassium iodide is colorless across the 700-350 nm spectrum, but when it interacts with iodine, the result is more than additive and an entirely new spectrogram appears. The absorption depends on the amount of iodine available to complex with the potassium iodide. Iodine, therefore, may be quantitated at this unique point, and its accurate determination will be unaltered by any variation in the iodide concentration. In a family of different equilibria (e.g., 0-20 ppm I_2), one maximum rises and the other falls as the equilibrium shifts, but the intersection (isosbestic) remains constant. In Figures 3 and 4, we see the iodine solutions become more transparent on the long wavelength side of the point as the KI is increased and less so on the short wavelength side. The symmetry of this effect is useful, since it permits us to use a wider bandpass filter in an iodine colorimeter than would otherwise be possible.
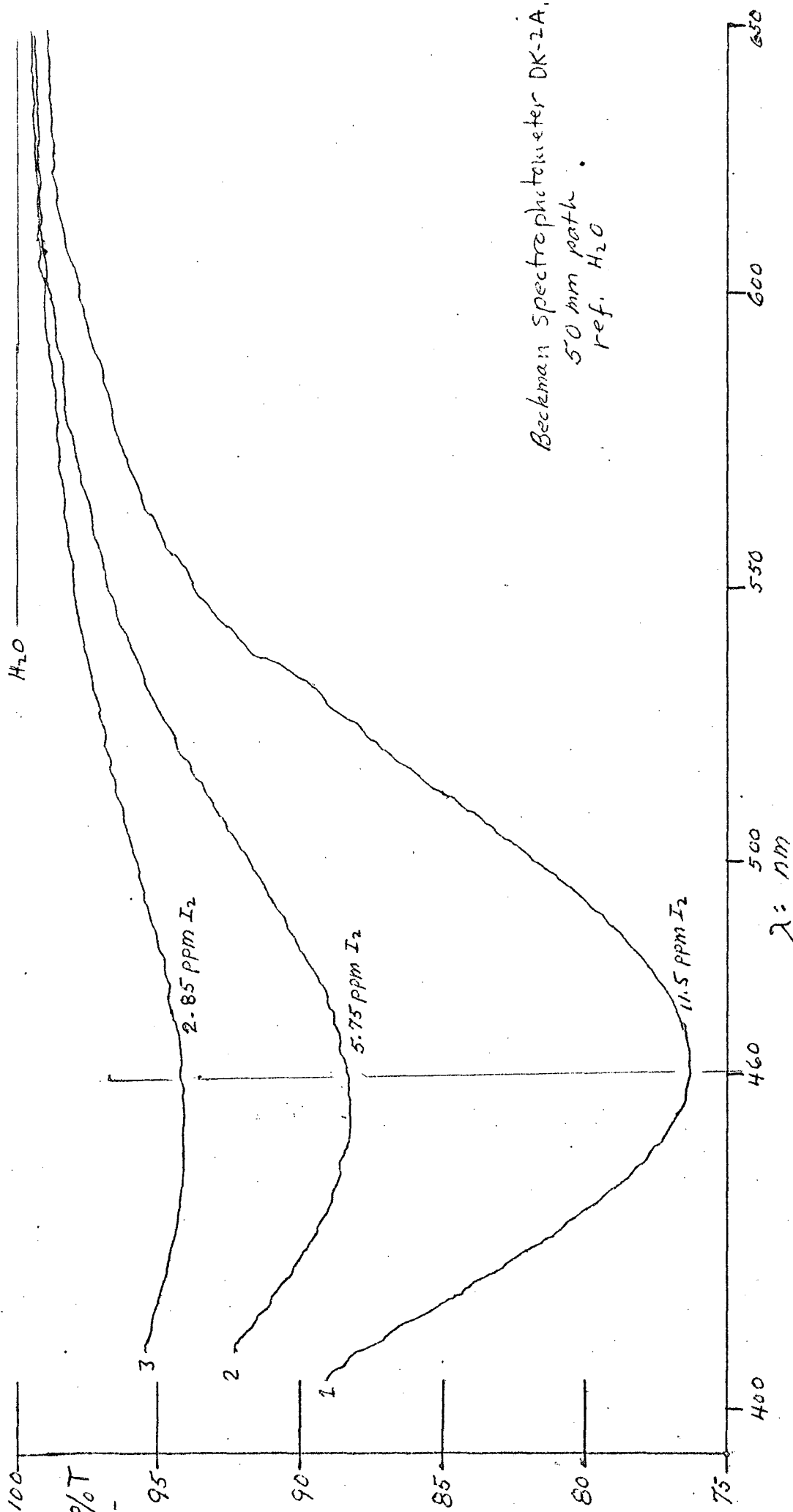
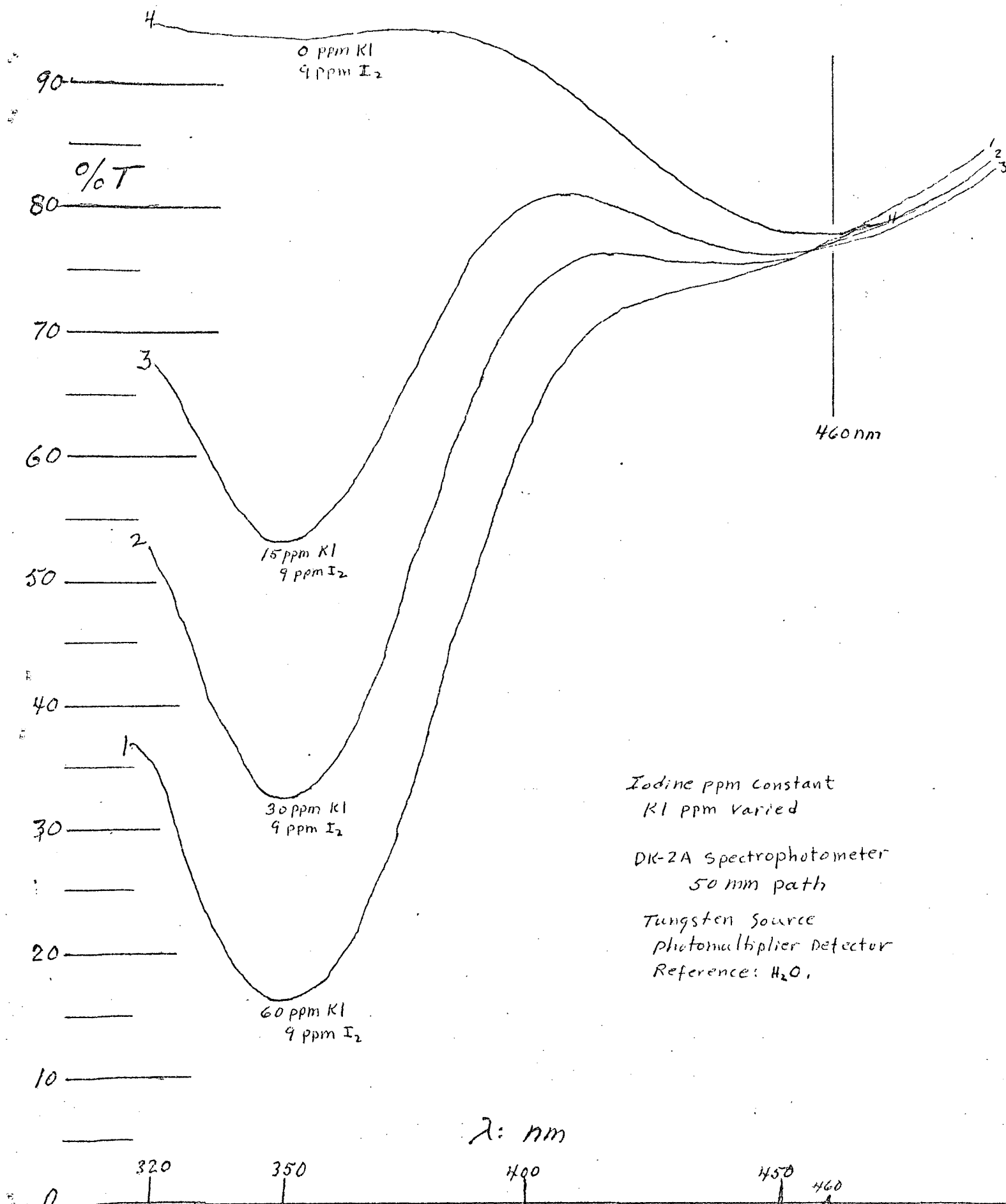Figure 1. Spectroscopic Scan of Aqueous Iodine

FR-1116-101

Figure 2. Iodine-Potassium Iodide Scans. I_2 content held constant.

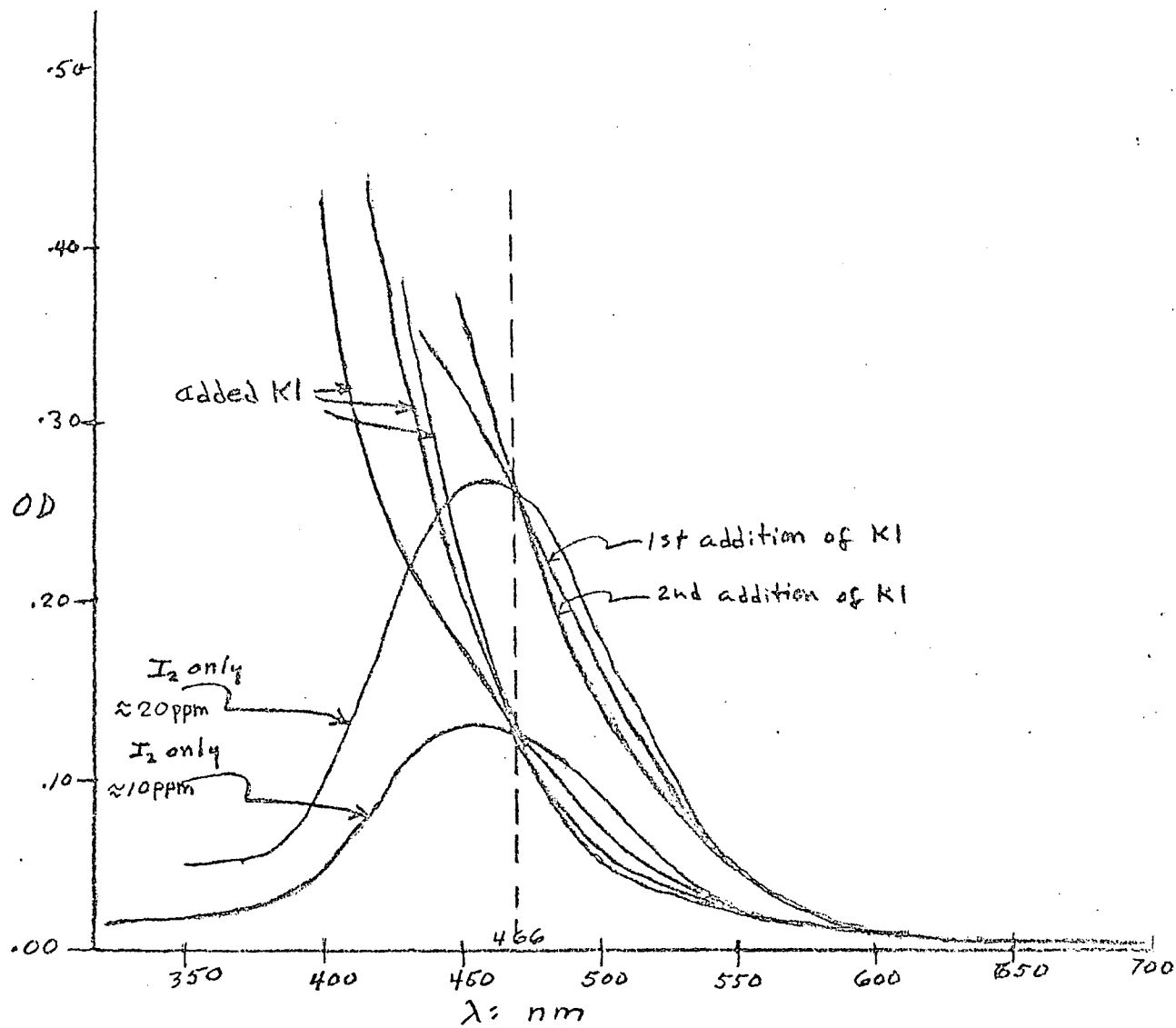Figure 3. ISOSBESTIC POINT for I_2-KI Solutions. Shown here in % Transmission Mode.

Figure 4. ISOSBESTIC POINT. The cross-over points are clearly shown
in this Absorbance Mode presentation.

That this is so was demonstrated by measuring I_2-KI solutions in two different colorimeters having much wider bandpasses than that of the DK Spectrophotometer (half bandwidth, at 460 nm, of only 0.2 nm). One colorimeter, a grating instrument (continuous spectrum), has a constant half bandwidth of 20 nm; that of the other instrument (eight filtered wavelengths) is 25 nm. The test results are shown in Figures 5 and 6. The agreement on the location of the isosbestic point for the spectrophotometer and the two colorimeters is indeed remarkable--considering the differences in the instruments. Even so, the exact location of this point has yet to be determined, and will have to await a careful check of the calibration of the DK Spectrophotometer. Although the bandwidth can be quite wide for the iodine filter, as the colorimeter tests proved, it is still important that it be centered at the isosbestic wavelength as a few nanometers either way will introduce error in the iodine extinction value.

In addition to the "iodine filter", the proposed iodine monitor will also require a "reference filter" in order to establish a "zero iodine" signal (one of two signals required for setting "span"). Figures 2 and 3 show that there is a "spectral window" from about 625 to 700 nm where iodine solutions show no significant absorption. This region, then, can be used in lieu of a reference cell. That it is suitable for this purpose is shown by the 700 nm curve of the Beer's Law plots in Figure 7. The other plots in Figure 7 show, in addition to conformity with Beer's Law, how the isosbestic point compares with the scans at 460 nm and 550 nm for aqueous iodine and iodine-iodide.

There are four standard expressions for the comparison of absorption intensities in current regular use. These formulae are defined and, substituting numerical values in the expressions, a value for iodine extinction at 467 nm is obtained:

1. ϵ = molar extinction

$$\epsilon = \frac{OD}{\text{path (cm) x molar conc}}$$

where: OD = 0.089 for 7 ppm I_2 (for example)

                  Path = 5.0 cm

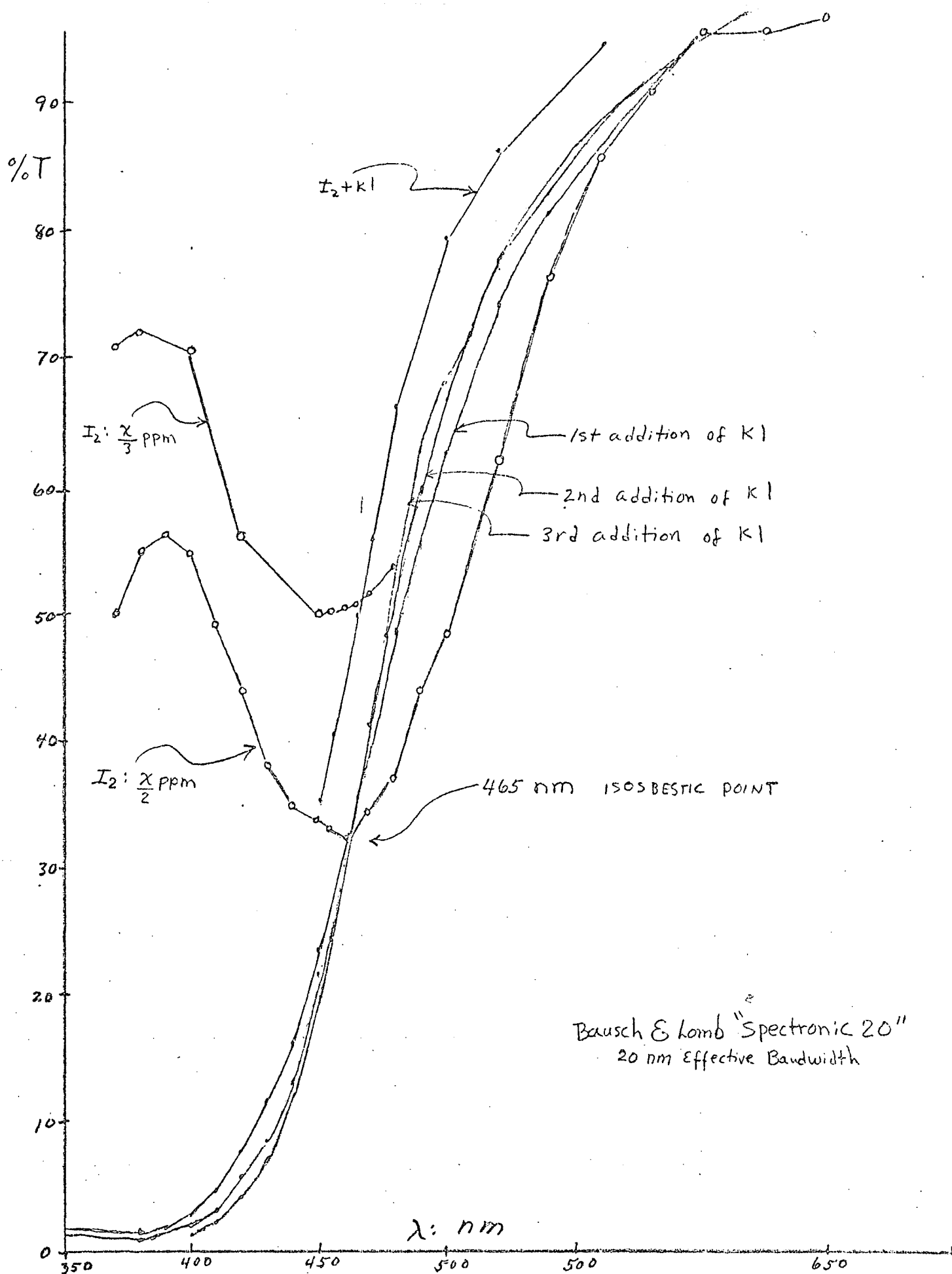   Molar Conc = 2.8×10^{-5} M

Figure 5. ISOSBESTIC POINT for a grating colorimeter. The bandwidth here is 100X that of the DK.
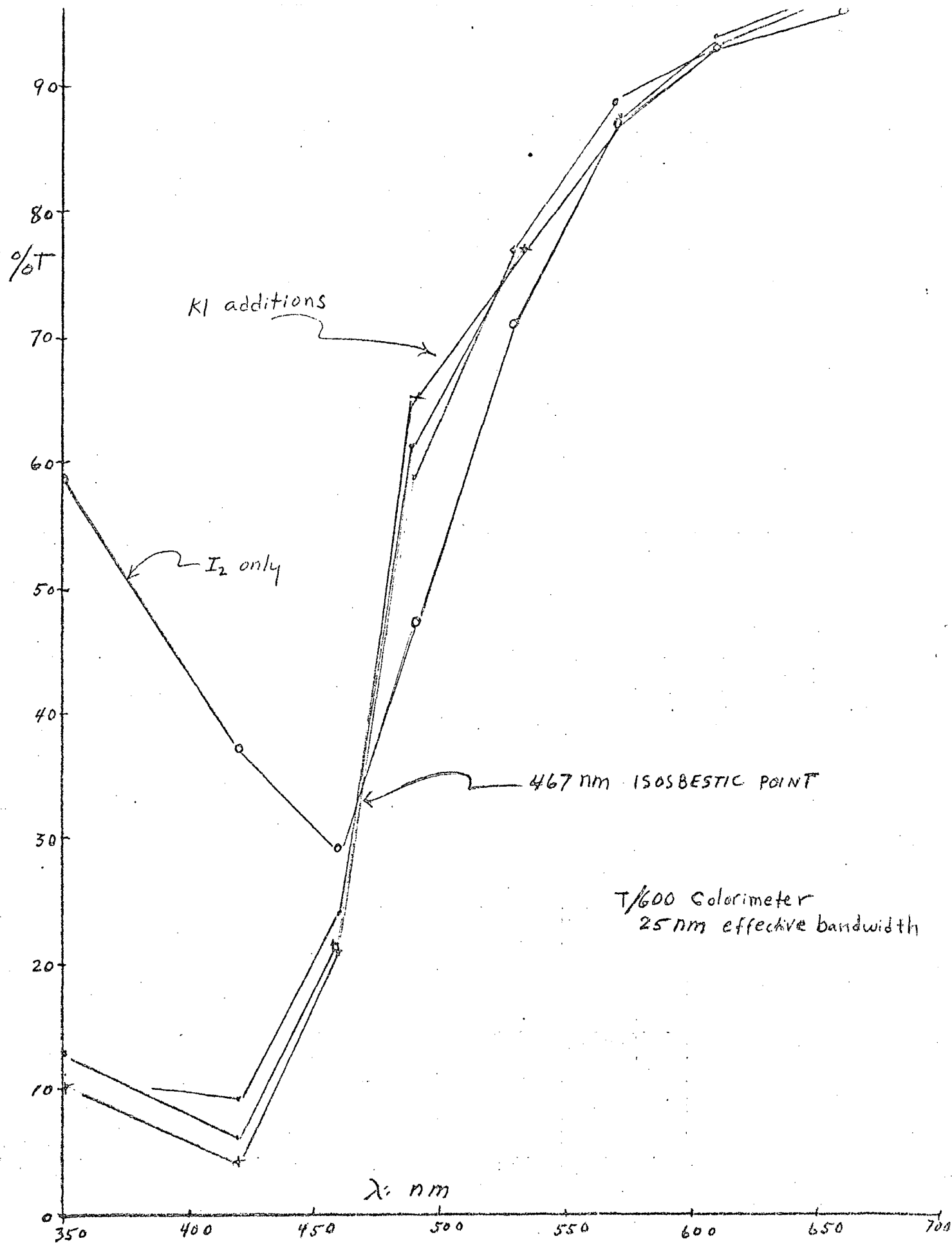
Figure 6. Although the simple colorimeter used here has but 8 wavelengths (filters), their distribution allows the isosbestic point to appear when data points are plotted.
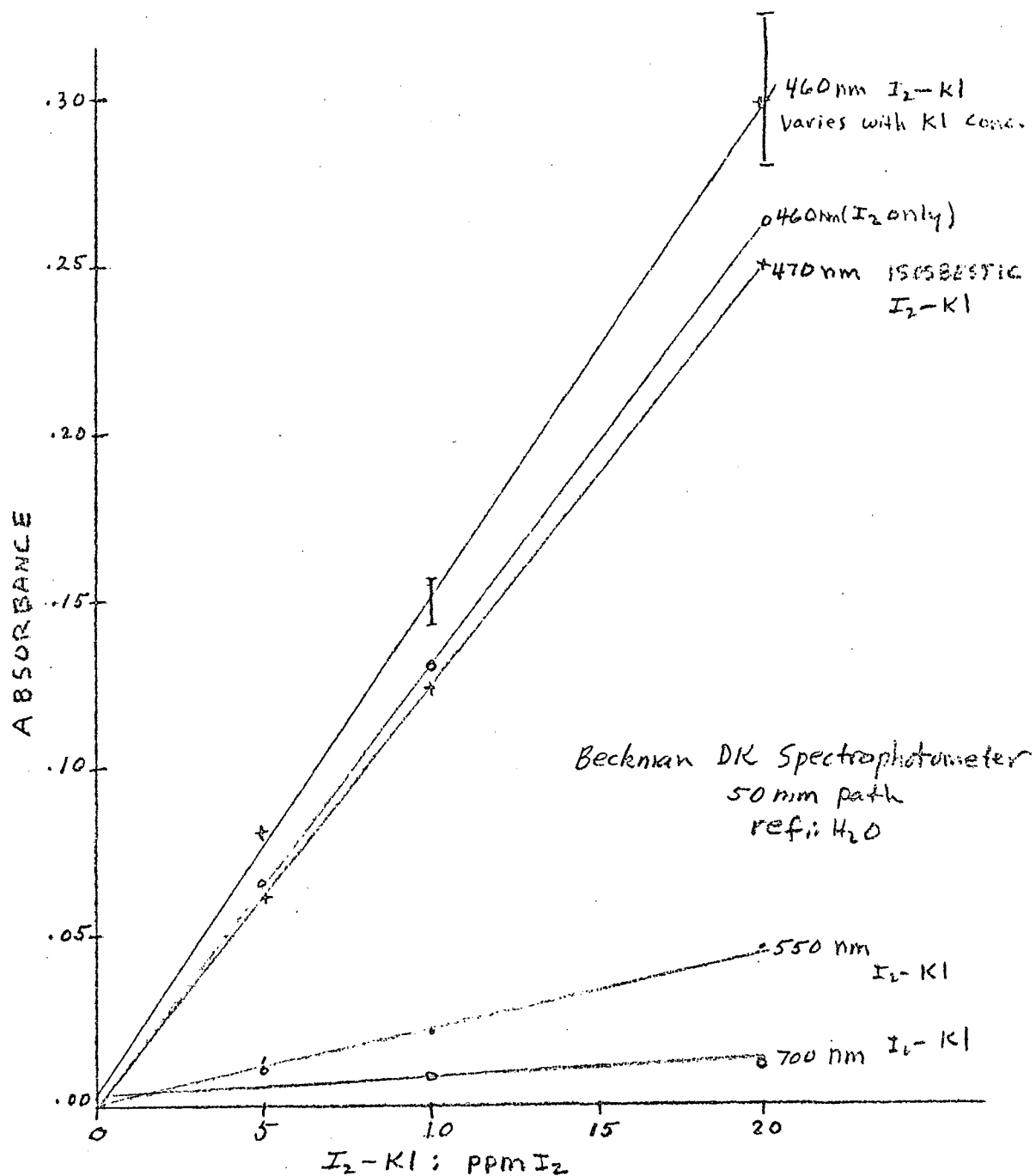
Figure 7. Absorbance Vs. Concentration (ppm I_2) at four wavelengths for
I_2 and I_2-KI solutions. Note that there is little loss of
sensitivity at 470 nm (isosbestic) compared with maximum
sensitivity at 460 nm.

Then, $\epsilon = \dfrac{0.089}{5 \times 2.8 \times 10^{-5}}$

$= 6.4 \times 10^2 \text{ 1/mol-cm}$

2. Log ϵ = logarithm (to base 10) of above

Log ϵ = log 6.4×10^2

$= 2.806$

3. E (1%, 1 cm) or E_1^1 or $E \frac{1\%}{1 \text{ cm}} \text{nm}$

$E \text{ (1\%, 1 cm)} = \dfrac{OD}{\text{path (cm)} \times \text{conc \% W/V}}$

$E = \dfrac{0.089}{5 \times 7 \times 10^{-4}}$

$= 25.4 \text{ cm}^{-1} \text{ \% W/V}^{-1}$

4. Specific α

$\alpha = \dfrac{OD}{\text{path (cm)} \times \text{conc g/liter}}$

Specific α differs from formula 3 in the concentration unit by a factor of 10 and therefore, in our example, specific α = 2.54.

3.0   TURBIDITY AND INTERFERENCES

Although the iodine-potassium iodide solutions are practically transparent in the "window region" (650-700 nm), the transparency here can be degraded if there should be enough particulate matter in the water. Since the lowered transparency (due to light scattering) would be evident across the entire spectrum, this source of error can be substantially eliminated electronically at the time the span is adjusted. The signal for 100% T bears a fixed ratio to zero percent transmission; thus, any change in %T at 700 nm is automatically adjusted by the circuitry to preserve the required ratio.

It is assumed that any turbidity arising from particulate matter in the water supply will have particle radii much longer than the light wavelengths

(700-470 nm). For this assumption, the scattered light energy is nearly independent of wavelength. In our turbidity experiments we found this to be so.

Figure 8 shows one experiment. Scans were made of an iodine-iodide solution with and without a little very fine soil in the solution. The spectrophotometer gain (%T control) was then increased to just compensate for the displacement of the two traces at 650 nm. A third scan was then made. The "adjusted curve" shows accurate tracking of the "without soil" scan from 650 to the iodine measuring wavelength (470 nm) where there is a negligible non-congruence. The manual adjustment performed in this experiment will be done electronically in an automated colorimeter.

In another interesting experiment, a silicone emulsion* provided a different species of turbidity. Figure 9 shows the results of applying the same procedures used in the previous experiment. Again, the "adjusted curve" shows good agreement with the "turbidity-free" scan. In both cases, the deviations at 470 nm represent an iodine error of less than 0.5 ppm.

Turbidity evaluations are rendered somewhat uncertain because of variable interactions between iodine and the turbidity agents. If the interaction is simply adsorption which removes some iodine from optical absorbance, then the colorimeter will still accurately measure the level of free iodine available for germicidal activity. Color changes resulting from the interaction would be a source of error, but we have not seen this happen with turbidity agents. Color changes are more to be expected in the interaction between iodine, iodide, and active chemical substances.

In the course of our previous iodine work we tested ten compounds for iodine interference. At concentrations below the maximum acceptable for potable water, we found no serious interference with the iodine determination. Our guide for these levels was "Water Management Results for the 90-Day Space Station Simulator Test" (MDAC paper WD1582, April 71, McDonnell-Douglas Corp.). This document

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*Dow-Corning Antifoam B Emulsion (10%).
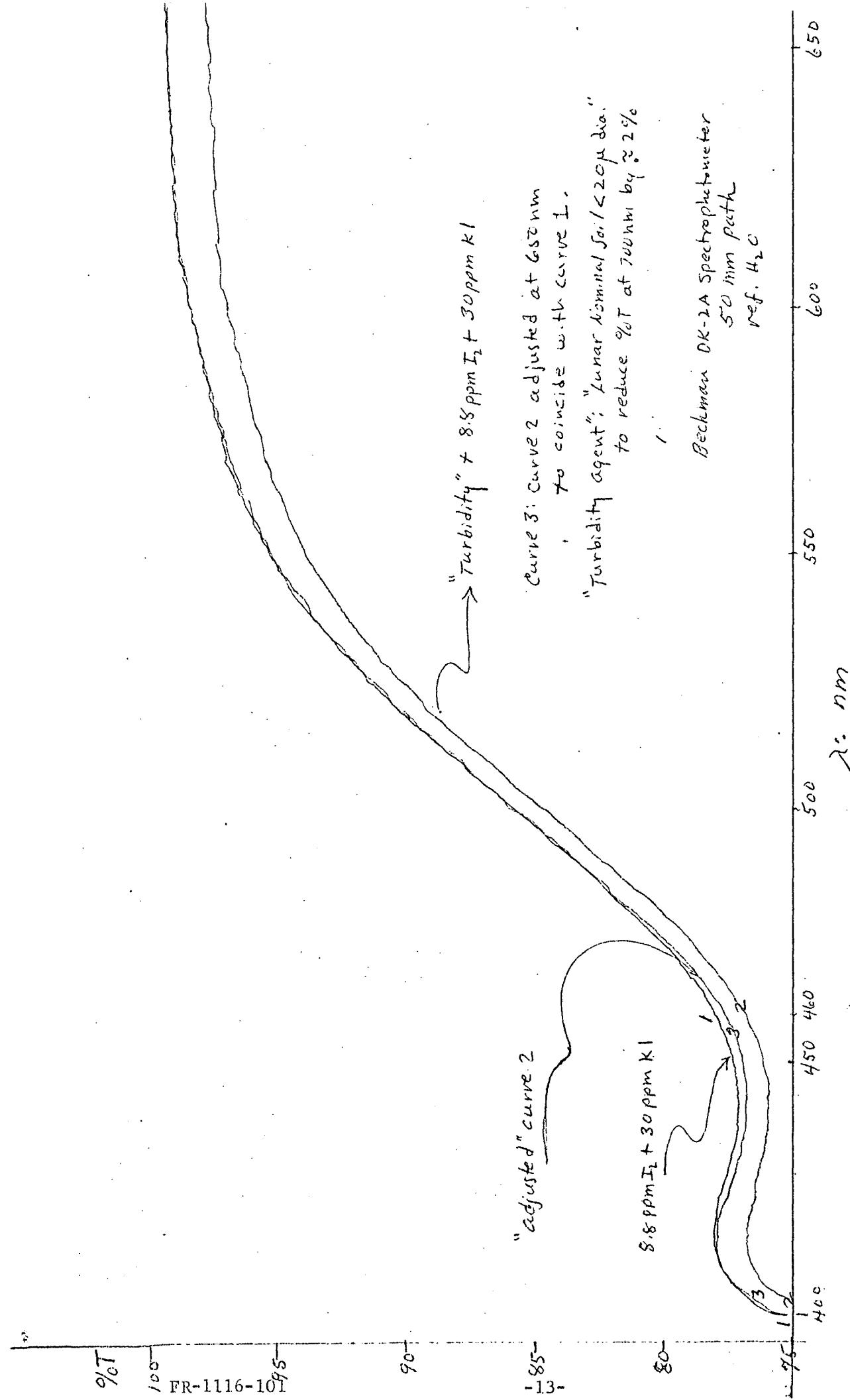
Figure 8. Interference Experiment. Turbidity produced by a species of soil in very fine particle form (50% <10μ dia.).

"Turbidity" + 8.8 ppm I₂ + 30 ppm KI

Curve 3: Curve 2 adjusted at 682 nm to coincide with curve 1.

"Turbidity agent"; "Lunar dismal Soil <2cm dia." to reduce %T at 700 nm by ≈ 2%

Beckman DK-2A Spectrophotometer
50 mm path
ref. H₂O

"adjusted" curve 2

8.8 ppm I₂ + 30 ppm KI

λ: nm

%T

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-13-

%T

100

95

90

85

80

75

H_2O

"Turbidity Agent": 10 µl Dow Corning® Antifoam B in 100 ml H_2O.

Curve 3: curve 2 adjusted at 650 nm to coincide with curve 1.

Beckman DK-2A spectrophotometer 50 mm path ref. H_2O

$8 ppm I_2 + 30 ppm KI$ + "turbidity agent"

$8 ppm I_2 + 30 ppm KI$

"Adjusted" curve 2

λ: nm

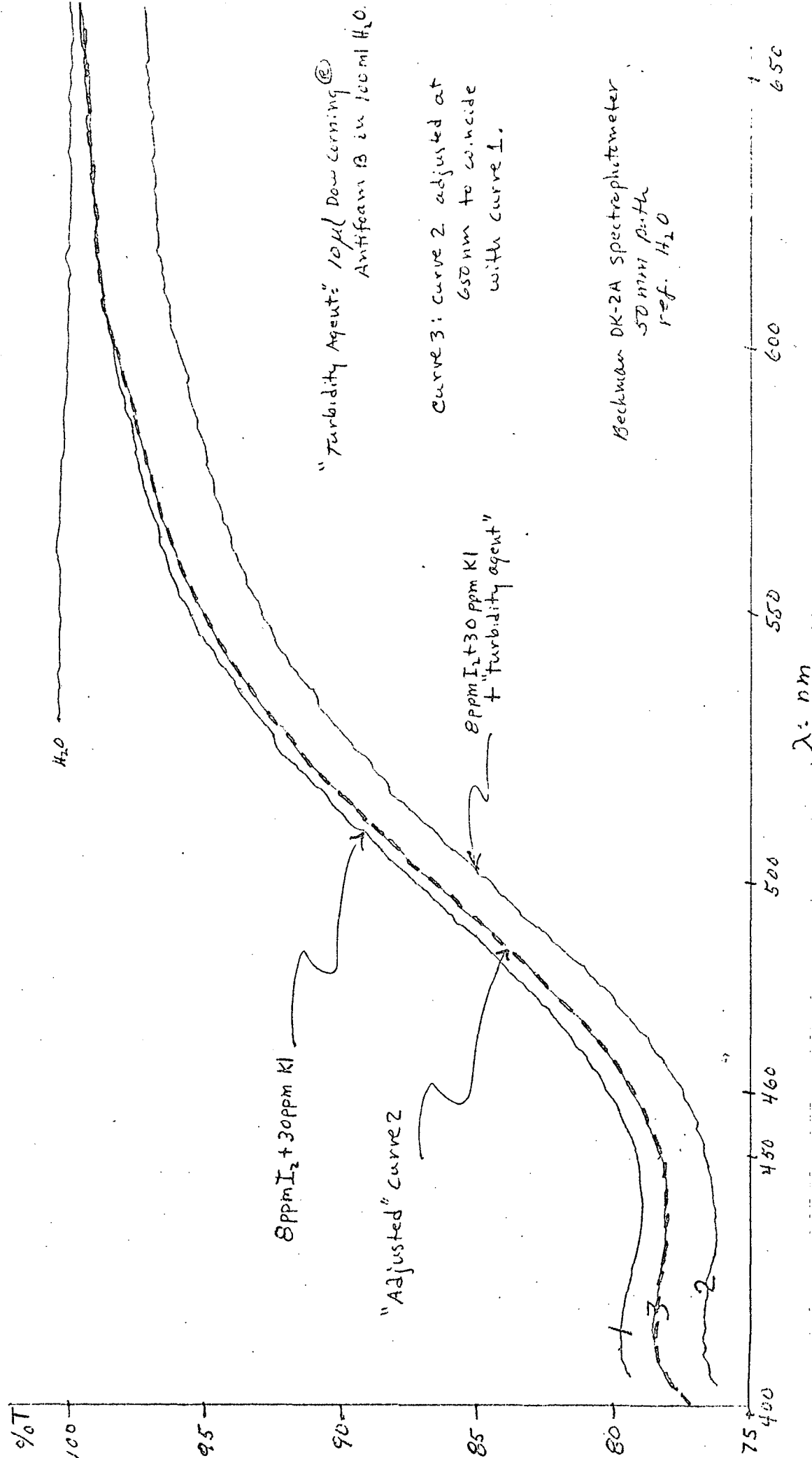400 450 460 500 550 600 650

Figure 9. Interface Experiment. Turbidity agents show a general absorption across the entire spectral range (700-400 nm).

reported test results for a large number of chemical substances in water. The concentrations found were generally much less than one part per million. Ferric chloride, in our work, showed the greatest effect. Figure 10 shows that this compound begins to absorb light below 550 nm and therefore would be expected to affect the iodine measurement. Figure 10 also shows that as much as 2 ppm $FeCl_3$ will not seriously affect the iodine readout. Curve 4 shows a scan of what is really an unrealistically high level (5 ppm) of $FeCl_3$ in the I_2-KI solution. An attempt to compensate for the displaced curve by the "adjustment" technique appears unsuccessful, but the chemistry of the reaction indicates that the iodine determination was probably correct:

$$2\ Fe^{+++} + 2\ I^- \rightarrow 2\ Fe^{++} + I_2$$
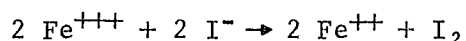
That is, if there is enough iodide present, the ferric ion is oxidized to ferrous with the formation of _more_ iodine! We have, in previous work, already observed that the ferrous ion, at low levels, does not color the solution or affect the iodine level. Chemistry also reports that the cupric ion is similarly oxidized to the cuprous state by reaction with iodide, again yielding iodine:

$$2\ Cu^{++} + 4\ I^- \rightleftharpoons 2\ CuI + I_2$$
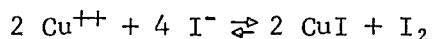
4.0   FLOW-THROUGH CELL

Since the planned Iodine Monitor has "on-line" status, it will have water flowing through it continuously (via a shunt), except for a brief period when iodine measurements are required. One of its components will, therefore, be a flow-through cell. Such a cell has been under test during most of the weeks of this project. Scrupulously clean cell windows are mandatory in accurate spectroscopy, but it would be difficult, if not impractical, to _maintain_ this condition in the flow-through cell. Fortunately, the colorimeter electrical system can compensate nicely for an appreciable degree of signal reduction caused by dirty cell windows. Of course, the generous path length for the sample (50 mm) helps to maintain an adequate signal to "this-species-of-noise" ratio.
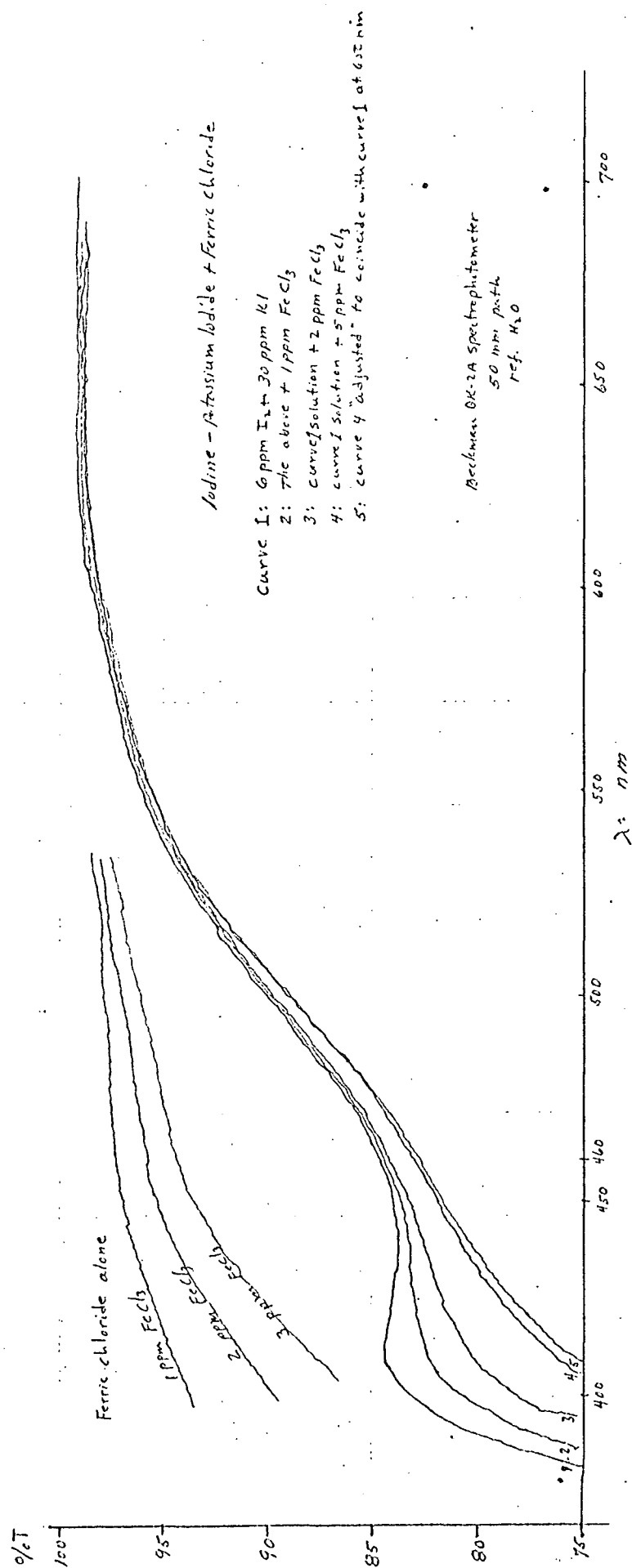
Figure 10. Interface Experiment. The effect of ferrif chloride (1-5 ppm) on the I_2-KI absorption band. FeCl3 does not begin to absorb until the scan falls below 550 nm.

In order to get some idea of how long a flow-through cell will be serviceable, the usual cleaning of the cell between samples was omitted over a period of several weeks. During this period, any fall-off in percent transmission was, of course, compensated by adjusting the gain control of the DK Spectrophotometer. At the end of the test period a final recording was made of the cell transmission using plain water as the sample. The cell was then thoroughly cleaned, filled with water, and another scan was recorded. Figure 11 shows that the difference in %T between "before" and "after" cleaning amounts to about two percent. This offset is easily compensated by the electrical system of any spectrophotometric instrument.

We have redesigned the flow-through cell for the planned colorimeter. The cell used in this project has the inlet and outlet ports set in slightly from the ends. The new design features inlet and outlets tangent to the windows. This geometry will allow a flow of water across the windows, which accomplishes two things: facilitates complete sample changing, and provides mechanical washing of the windows. Our tests suggest that throughout the longest mission any decreased window clarity will not exceed the compensatory capability of the electronic system.

5.0   MECHANICAL-OPTICAL SYSTEM

Figure 12 shows the general construction features of a small, rugged, single-beam iodine colorimeter prototype based on our Preliminary Design concepts. The functional optical components are, in succession: a tungsten lamp source, a source lens, a filter wheel (two filters), a flow-through sample cell, a detector lens, and a PIN Silicon Photodiode detector (usable wavelength range from 400 to 1100 nm).

The source lens images the radiant tungsten filament directly on the detector lens so that the image nearly fills the 10 mm square opening and aperture stop in front of the detector lens. This requires that the source lens magnification be 5.6X (for a filament of 1.8 mm^2). The source is a tungsten lamp with a 1-inch diameter bulb. At 28 Vdc and 0.2 A it will require approximately 6 watts (filament temperature will be 2700°K). The rather large bulb has been selected
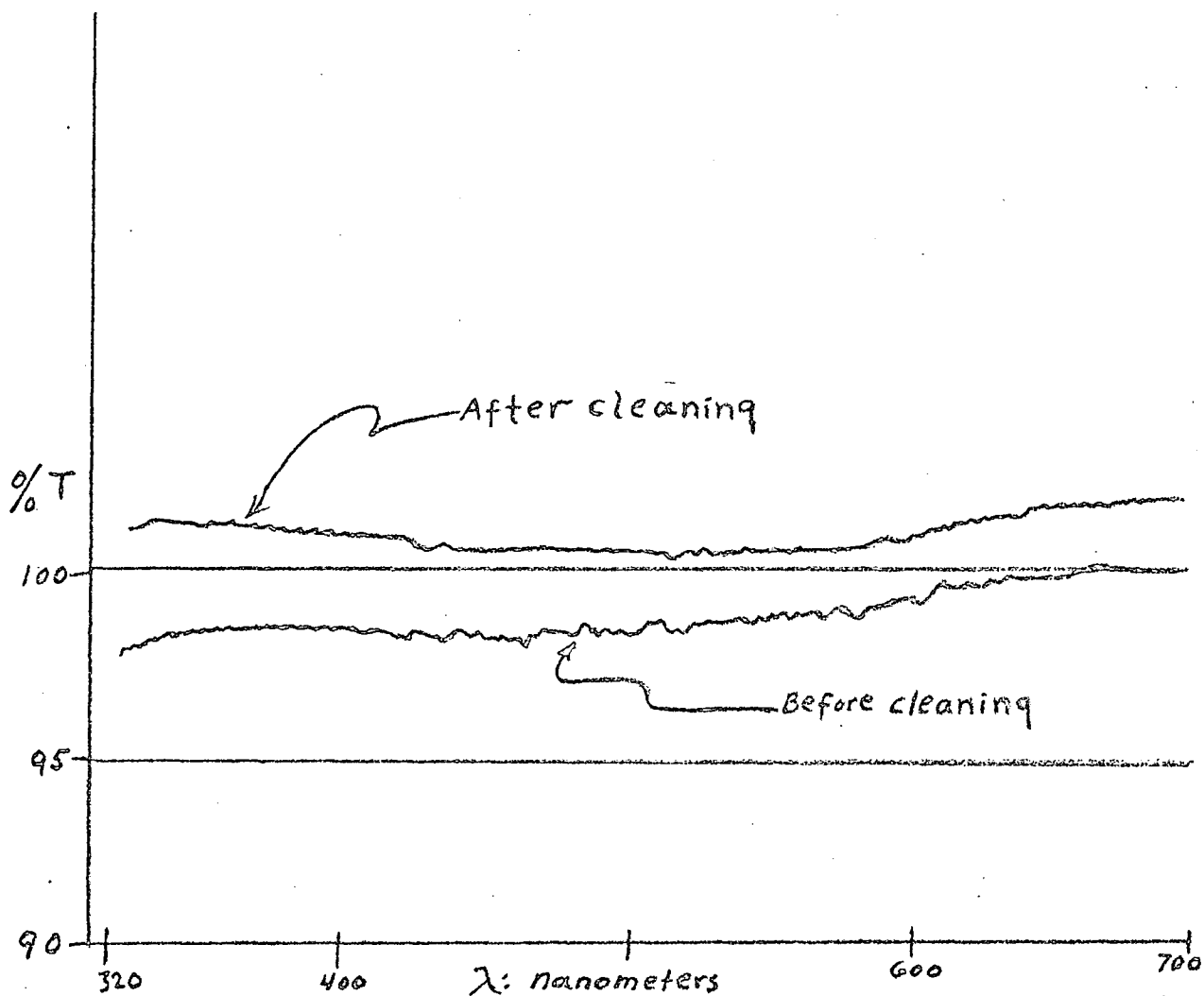
Figure 11. FLOW-THROUGH CELL. The cell was used for many I_2-KI samples over a period of several weeks. Cleaning between samples was omitted. The "before cleaning" sample was H_2O. The cell was cleaned and H_2O filled. The spectral response for the two samples is shown here.
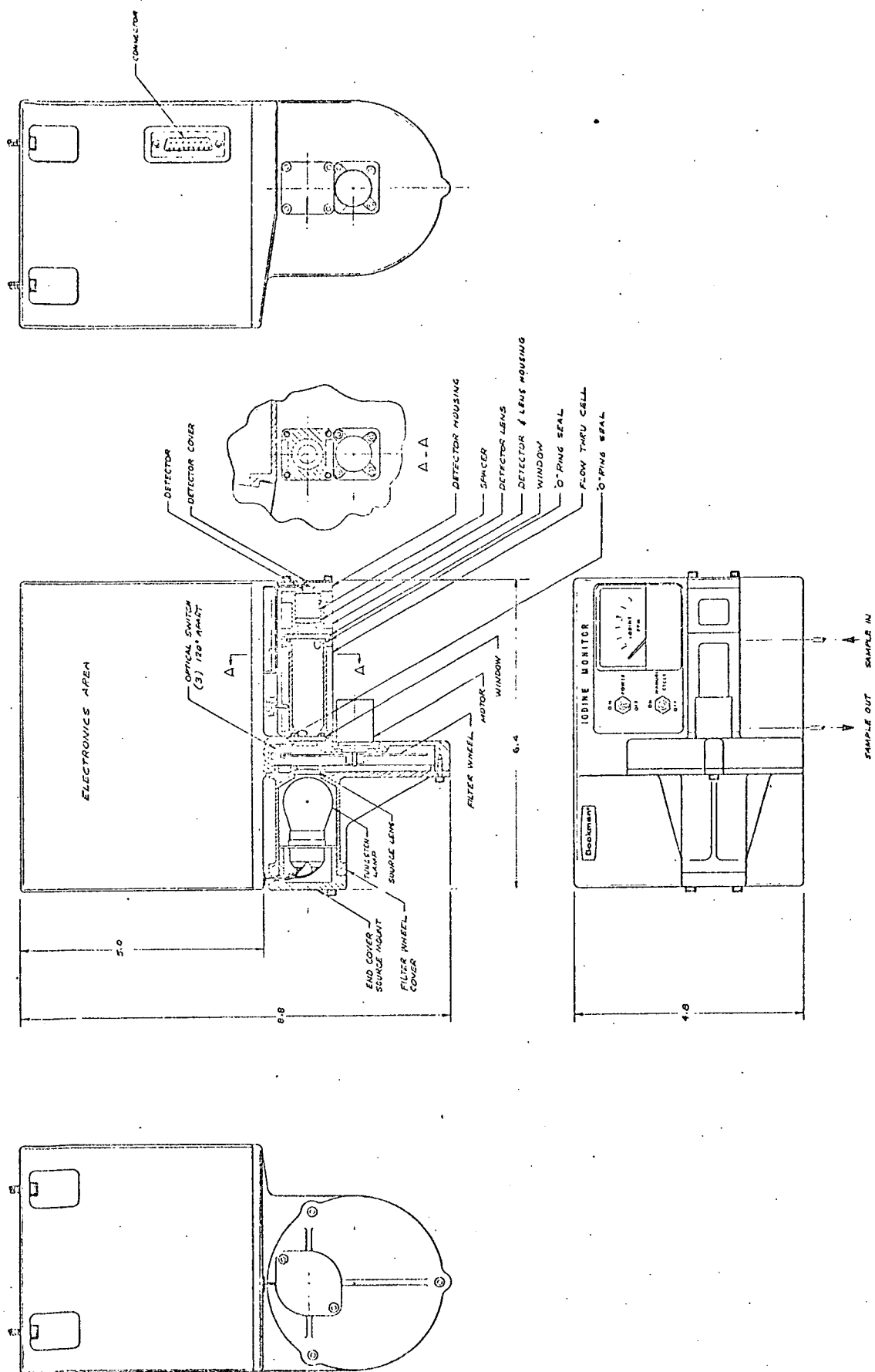
Figure 12. Mechanical Layout of Iodine Monitor

because of its sturdiness, and the large envelope volume causes the tungsten coating of the inside of the bulb to occur more slowly.

The detector lens images the 10 mm square aperture stop at the source lens directly on the sensitive area of the detector with a 1/5.6X magnification. This two-lens system provides excellent stray light control because the optical geometry prevents the detector from "seeing" areas outside the maximum ray boundaries.

The filter wheel, sketched in Figure 13, carries two filters: a "reference" filter for light transmission at 650 nm, and a "sample" filter for transmitted light at 467 nm. The "notch" in the wheel permits energy from three light-emitting diodes to fall upon three photodetectors used to provide position references for controlling the signal phase adjustment (Figure 14). The filter wheel is rotated by a small stepping motor. The electrical system is discussed in a following section of this report.

All the components of this system can be rigidly mounted on machined and lapped surfaces of an aluminum (or magnesium) casting or machined housing (Figure 12). The rigid mounting will permit the instrument to withstand high g forces and severe vibration loads without damage or misalignment of optical elements. One design concept for housing this instrument is shown in Figure 15. As shown, the overall dimensions are: width 6-3/8 inches, height 4-3/4 inches, and overall depth 8-3/4 inches. The weight can be held well under three pounds.

Figure 15 shows two switches on the front of the housing. These are the only controls, and normally will not be used. The power switch simply turns the +28 V primary power to the instrument on or off.

The Manual Switch initiates or terminates a manually-imposed duty cycle on the automatic sequencing mode of the system (it does not interrupt it). This switch has a center-off position and two momentary positions. In the "start" position (momentary), the manual cycle is initiated. If, during the manual cycle, the switch is placed in the "off" position (momentary), the manual cycle is terminated. If, however, the unit is put into the manual mode and
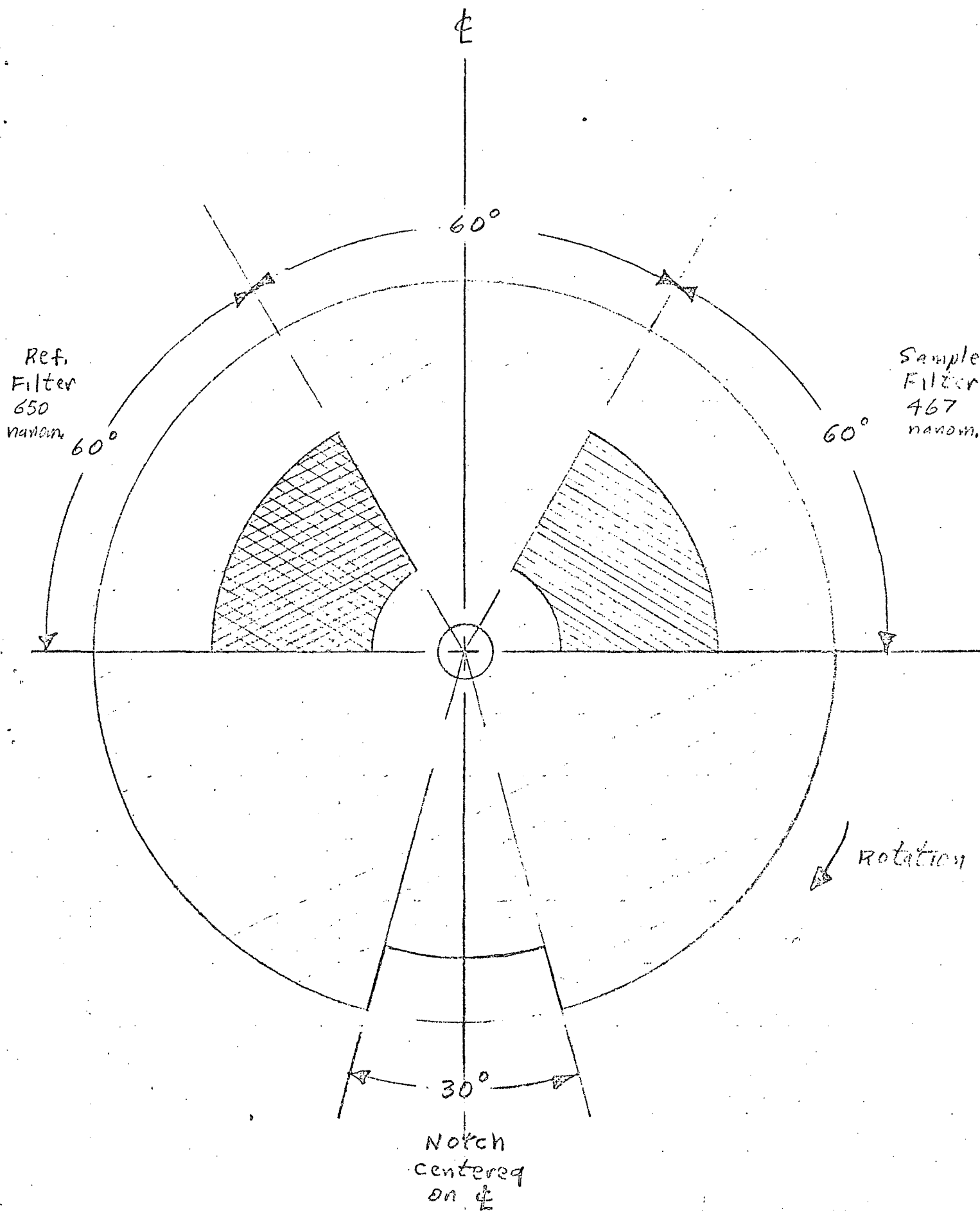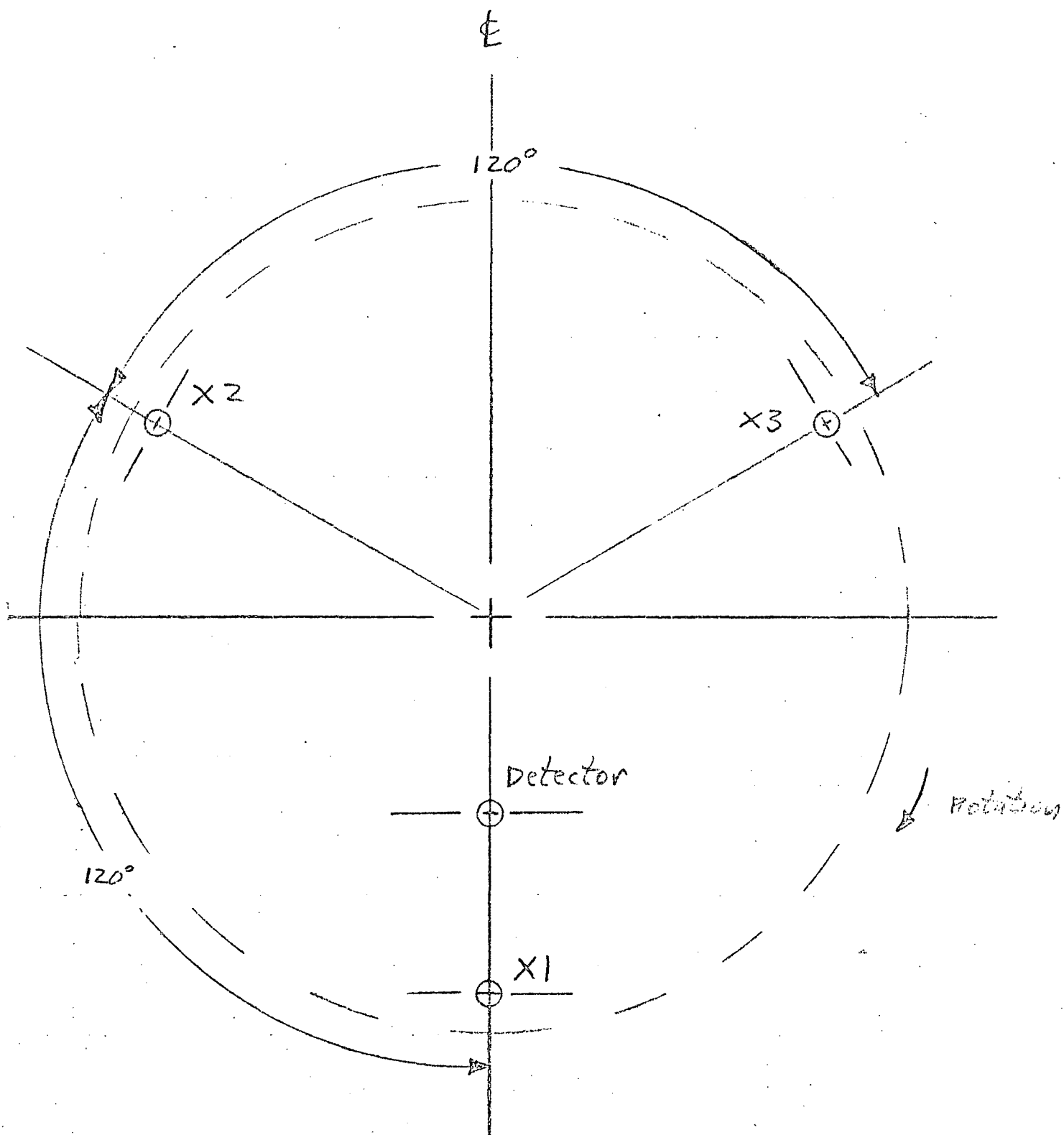
Figure 13.   Filter Wheel Iodine Monitor

Figure 14. Locations of Detector and
Wheel Sync. Decoder Pairs

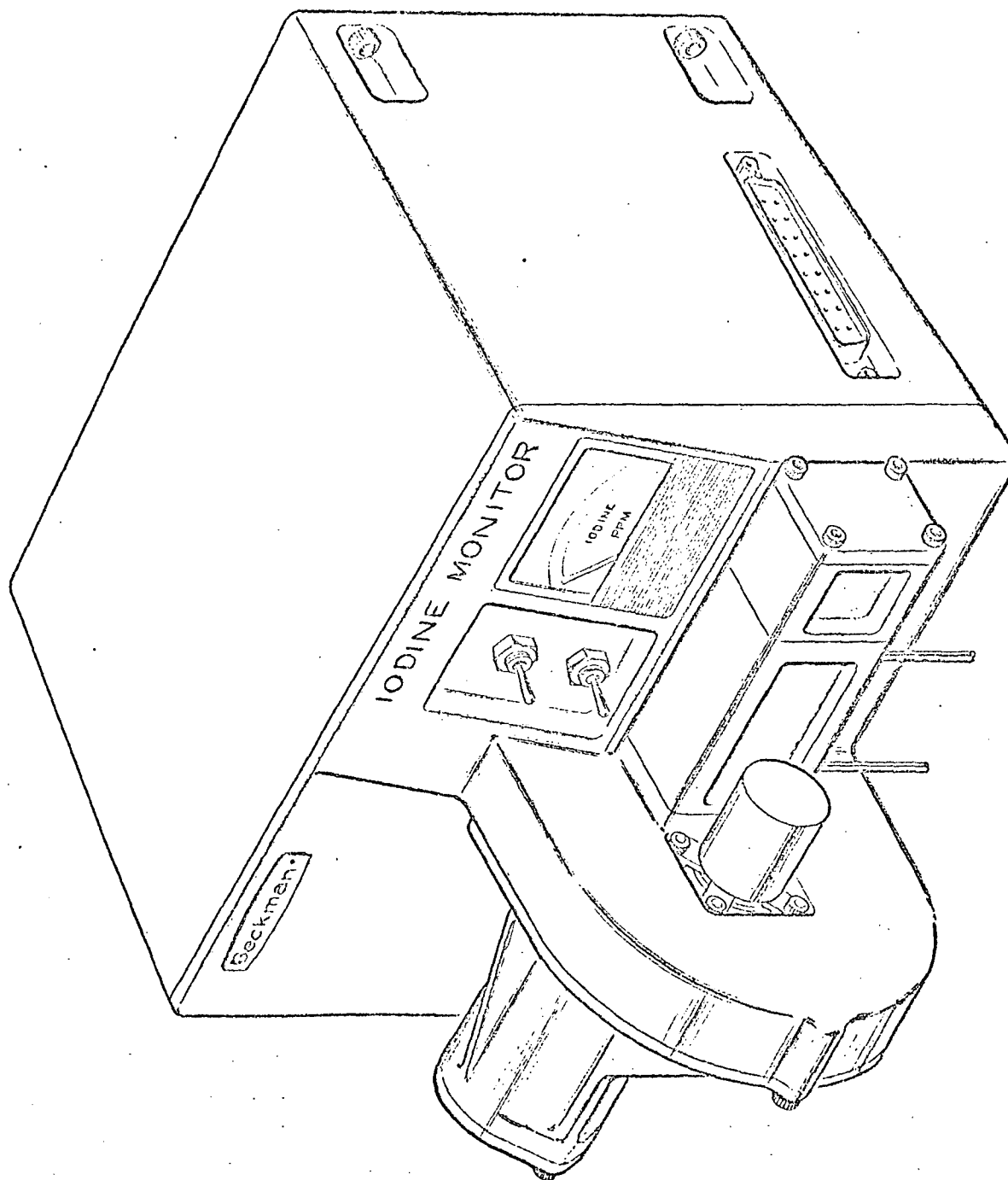X1 thru X3

= wheel sync.
decoder pairs.

Figure 15. Iodine Monitor

the manual switch is never placed in the "off" position, the manual cycle will continue for ten minutes and then shut off, unless the monitor has gone into the "periodic auto cycle."

The Preliminary Design features ease of disassembly for cleaning and replacement (or change) of components. Reassembly will maintain accuracy of component alignment without special tools or fixtures.

Instead of the conventional all-glass sample cell, our design will incorporate a metal shell and special glass window assembly fabricated to withstand 60 psia. Self-cleaning of the cell, especially the windows, will be facilitated by the tangential, spiral flow of the solutions from inlet to outlet creating a wiping action on the cell windows and walls.

6.0   ELECTRONICS FOR THE IODINE MONITOR

The spacecraft water supply will eventually require an automatic feedback control system which will sample the iodine content of the water and add iodine, as required, to maintain a predetermined level. Thus, two main components of the control system will be the iodine monitor and the iodine generator. In general, the monitor determines when to sample; it then generates a signal proportional to the iodine content and feeds this information to the generator which adds the required amount of iodine. This system must operate automatically and unattended for long periods of time, so it should not require periodic maintenance or calibration.

Such a system imposes certain restrictions on the iodine monitor electronics, which must be small, lightweight, rugged, reliable, and low in power dissipation. These goals of design are best achieved by utilizing solid-state circuits. The use of discrete semiconductors and preferably integrated circuits greatly decrease size and weight, and also enhance reliability. The use of MIL approved, screened components, properly derated and in ceramic packages, improves reliability even more.

6.1   Functions of the Electronics

The functions of the iodine monitor electronics may be broken down specifically into the following categories:

1. Measure the amount of iodine in the water and produce an analog signal, 0 to +5 volts, corresponding to 0 to 20 ppm of iodine. The electronics will automatically compensate for source lamp variations, water turbidity, etc.

2. Periodically turn on the iodine monitor, allow a warm-up period, close the inlet valve, and measure the iodine content--while at the same time alerting the iodine generator (by means of a relay contact closure) and sending it the analog signal. The sampling frequency will be easily programmable over a wide range. During the sample sequence, the meter on the iodine monitor will display the iodine content in ppm.

3. Respond to a manual input, turn on and display the iodine content on the meter, but without sending a signal to the iodine generator. This function will not interfere with the periodic sample sequence.

The iodine monitor electronics diagram is shown in Figure 16.

The electronics may also be divided into two very broad areas:

1. Measurement
2. Timing and power control

Each of these two areas will be discussed in turn. Available choices are explored and reasons are given for the approach which was selected.

6.2   Measurement Electronics

The heart of the measurement system is the filter wheel, containing two filters--one at a reference wavelength of 650 nm and the other at a sample wavelength of 467 nm. The tungsten source lamp sends light through both the sample and the filter wheel, where it is then picked up by the detector.
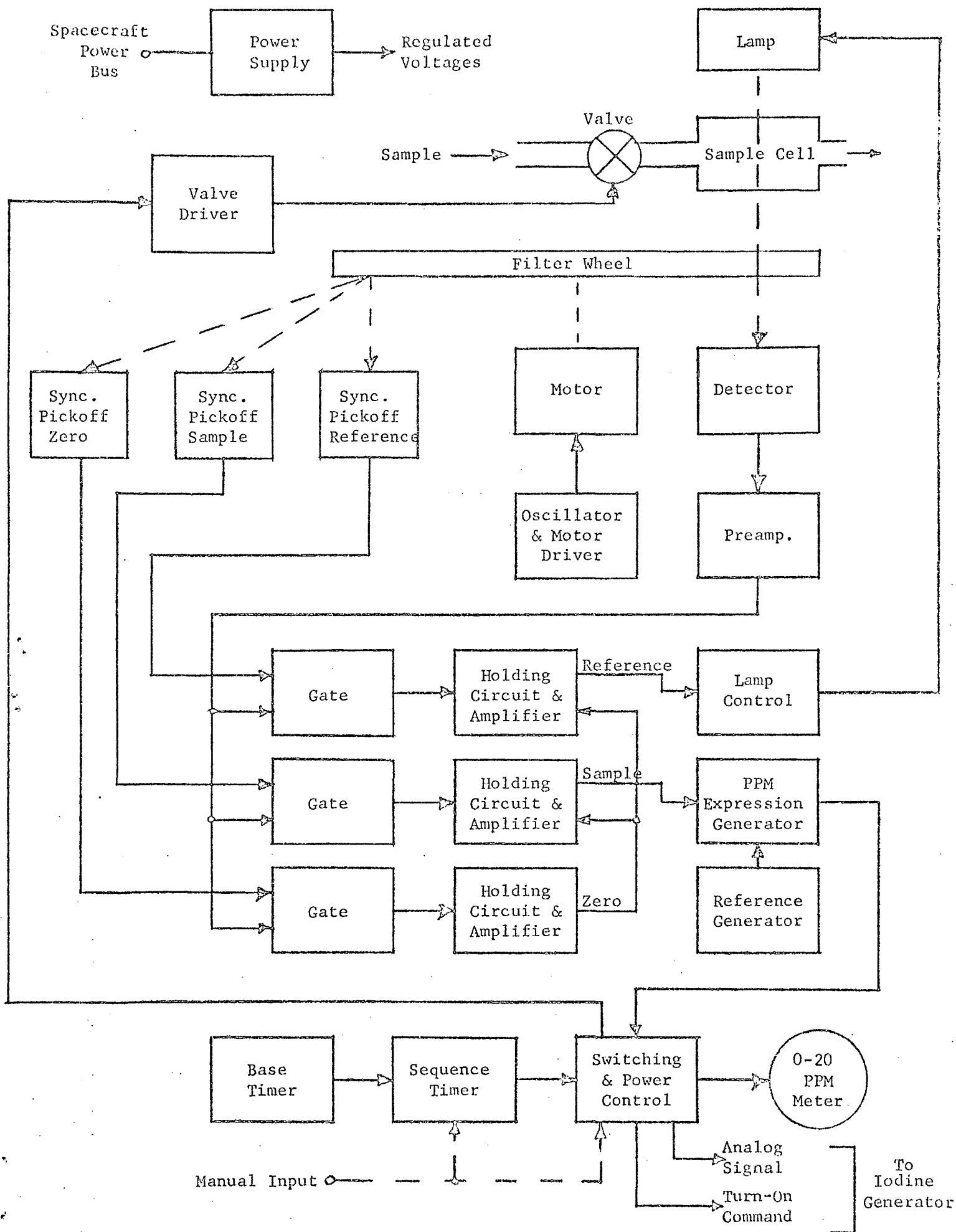
C

Figure 16.. Block Diagram, Iodine Monitor

Figure 13 shows the general layout of the filter wheel with the sample and reference filters. It might be considered that the wheel really has a third filter--the zero offset filter--through which no light is passed, but where a zero offset can be measured by the electronics.

The notch on the outer rim operates three optical switches which serve to pick up information about where the wheel is in its rotation cycle (or actually reveals which filter is in front of the detector at a given time).

Figure 14 shows the relative locations of the detector and optical switches.

Figure 17 relates Figures 13 and 14 and shows the signals at the optical switch outputs (X1 through X3) and the detector as a function of time. After the signal from the detector is amplified (by the preamp), it is fed through three FET switches to three holding circuits. The FET switches are operated by the outputs of the optical switches, such that the holding circuits have outputs corresponding to reference, sample and zero offset.

Since the light transmission, sample path and detector are highly critical parts of the system, the next section shows the specific considerations which went into the choice and use of the detector.

o <u>Calculation of Signal to Detector</u>

<u>Radiant Flux from Tungsten Filament</u>:

$$P_\lambda = \frac{A_n}{F_s^2} N_\lambda (\Delta\lambda) (T_\lambda^n)^3 T_\lambda^c T_\lambda^f \tau A_s T_\lambda^s \text{ watts}$$

N_λ = Spectral radiance of filament in watts/cm^2/μ-str.

3.0 watts/cm^2/μ-str. at 0.46 μ $\Big\}$

9.0 watts/cm^2/μ-str. at 0.65 μ $\Big\}$ Tungsten filament at 2700 °K

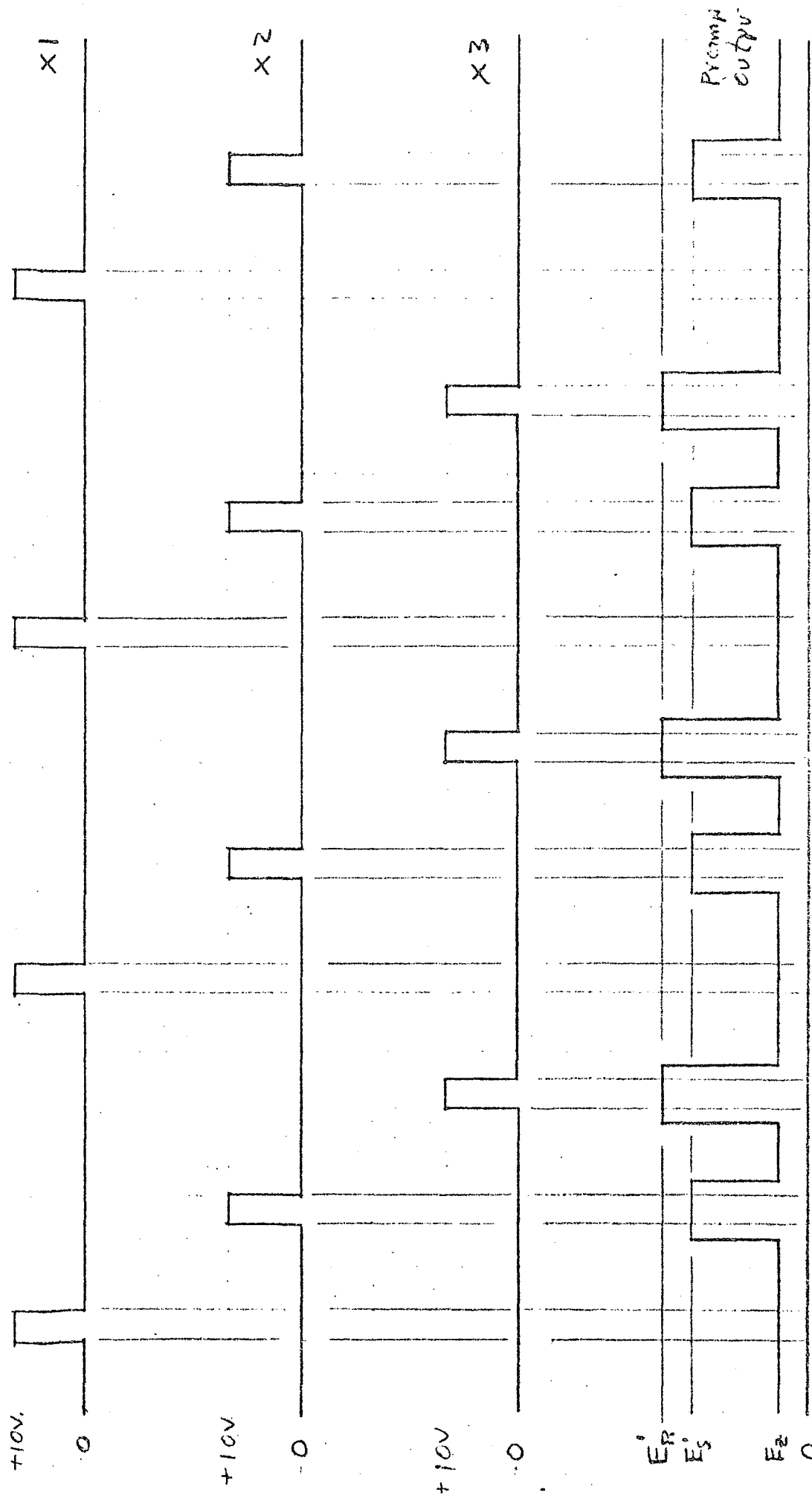$(\Delta\lambda)$ = Spectral bandpass in μ

= 0.04 μ

Figure 17. Output Waveforms

X1 High = Zero offset Sample switch on

X2 High = Sample Sample switch on

X3 High = Reference Sample switch on

T_λ^n = Transmission of each of the two lenses and single source envelope

= 0.87

T_λ^c = Transmission of H_2O without iodine in solution (50 nm optical path)

= 0.94

T_λ^f = Transmission of either filter

= 0.6

τ = Period of illumination during each filter cycle

= 1.0   Consider peak power

A_s = Effective area of tungsten filament

= 0.011 cm^2

A_N = Effective area of source lens

= 1.0 cm^2

F_s = Focal distance of tungsten filament from source lens

= 1.5 cm

T_λ^s = Transmission of iodine (applies only at sample λ = 0.46 μ)

= 1.0   0 ppm of iodine

= 0.536   20 ppm of iodine

Flux to detector at ref λ = 0.65 μ:

$$P_\lambda^R = \frac{1}{(1.5)^2} (9) (0.04) (0.87)^3 (0.94) (1.0) (.011)$$

= 1088 μ watts

<u>Flux to detector at sample λ for 0 ppm</u>:

$$P_\lambda^{\underline{s}} = \frac{1}{(1.5)^2} \ (3) \ (0.04) \ (0.87)^3 \ (0.94) \ (1.0) \ (0.011) \ (1.0)$$

$$= 364 \ \mu \ \text{watts}$$

<u>Flux to detector at sample λ for 20 ppm</u>:

$$P_\lambda^{\overline{s}} = P_\lambda^{\underline{s}} \times 0.536 = 196 \ \mu \ \text{watts}$$

o <u>Choice of Detector Type</u>

Six general types of detectors are considered:

1. Photo Emissive
2. Photoconductive (bulk effect)
3. Phototransistor
4. Photovoltaic (junction)
5. Photoconductive Shottky Barrier (junction)
6. Photoconductive-Diffused (junction)

The following criteria are most important for the iodine monitor's detector:

1. Visual response
2. Lifetime stability
3. Linearity
4. Ruggedness
5. Responsivity
6. Power consumption
7. Speed

Using the above information, it appears, in general, that the Shottky Barrier and the Diffused types are best for this application.

● <u>Choice Between Shottky and Diffused and Modes of Use for Detector</u>

Either type of detector may be used in either the Photovoltaic or the Photoconductive mode. The following table compares specific parameters:

Parameter	Shottky		Planar Diffused	
	Photovoltaic	Photocond.	Photovoltaic	Photocond.
Responsivity variation with temp. for $\Delta T = 50\,°F$	$-0.3\%/\,°F$ -15%	$\pm 0.07\%/\,°F$ $\pm 3.5\%$	$\pm 0.05\%/\,°F$ $\pm 2.5\%$	$+0.07\%/\,°F$ $+3.5\%$
Responsivity variation with λ at 467 versus 650 nm	$0.22/0.28$ $= 0.79$	$0.22/0.28$ $= 0.79$	$0.11/0.21$ $= 0.52$	$0.11/0.21$ $=0.52$
Dark Current Variation	No Dark Current	Doubles Every $+10\,°F$	No Dark Current	Doubles Every $+10\,°F$
Linearity	Good (R_L) Poor $(\overline{R_L})$	Good	Good (R_L) Poor $(\overline{R_L})$	Good
Response Time	microseconds	10 ns	microseconds	10 ns

The planar diffused detector, operated in the photovoltaic or unbiased modes, gives the least variation with temperature, although any temperature variations would be taken care of by the constant reference system.

No dark current is present in this mode. Speed of response should not be a problem, since the preamplifier output will be sampled after the detector has settled down.

Best linearity is achieved by running the detector at zero bias and operating the first stage in a current input mode.

If too much incident power strikes the detector, its response becomes non-linear, and linearity is of primary concern. In the reference mode, 1088 μW strike the detector, with an effective area of 8×10^{-3} cm^2, giving 136 mW per square centimeter. For linearity, power density on the PIN-040B should be less than 1 milliwatt per square centimeter. This can be remedied by a filter to cut down the light. A filter which cuts the light to 0.0027 of its original value will be used. This reduces the peak intensity to 0.367 mW/cm^2.

Power levels on the detector will now be:

Reference:	3 μW
Sample, 0 ppm:	1 μW
Sample, 20 ppm:	0.55 μW

S/N for sample 20 ppm will be:

$$S/N = \frac{psig}{N.E.P.} = \frac{5.5 \times 10^{-7}}{9 \times 10^{-14}} = 6.1 \times 10^6$$

o **Expression Generator**

After the three desired quantities (reference, sample and zero) are obtained in the holding circuits, they must be processed to obtain the correct analog signal (0 to +5 V) corresponding to the sample strength (0 to 20 ppm). The expression generator consists of several operational amplifiers which add, subtract, and multiply the three input quantities to obtain the analog signal. The process is greatly simplified by keeping the reference signal at a fixed value. This is done by means of a feedback system to control the source lamp. This also cancels out any variations due to water turbidity or blackening of the lamp envelope.

The analog signal obtained is not really quite linear (see Figure 18). This is due to the non-linear, light-filtering properties of iodine in water. For example, if 10 ppm of iodine in water allows K% of light through, then 20 ppm does not allow $\frac{K}{2}$ percent through, but K^2 percent.
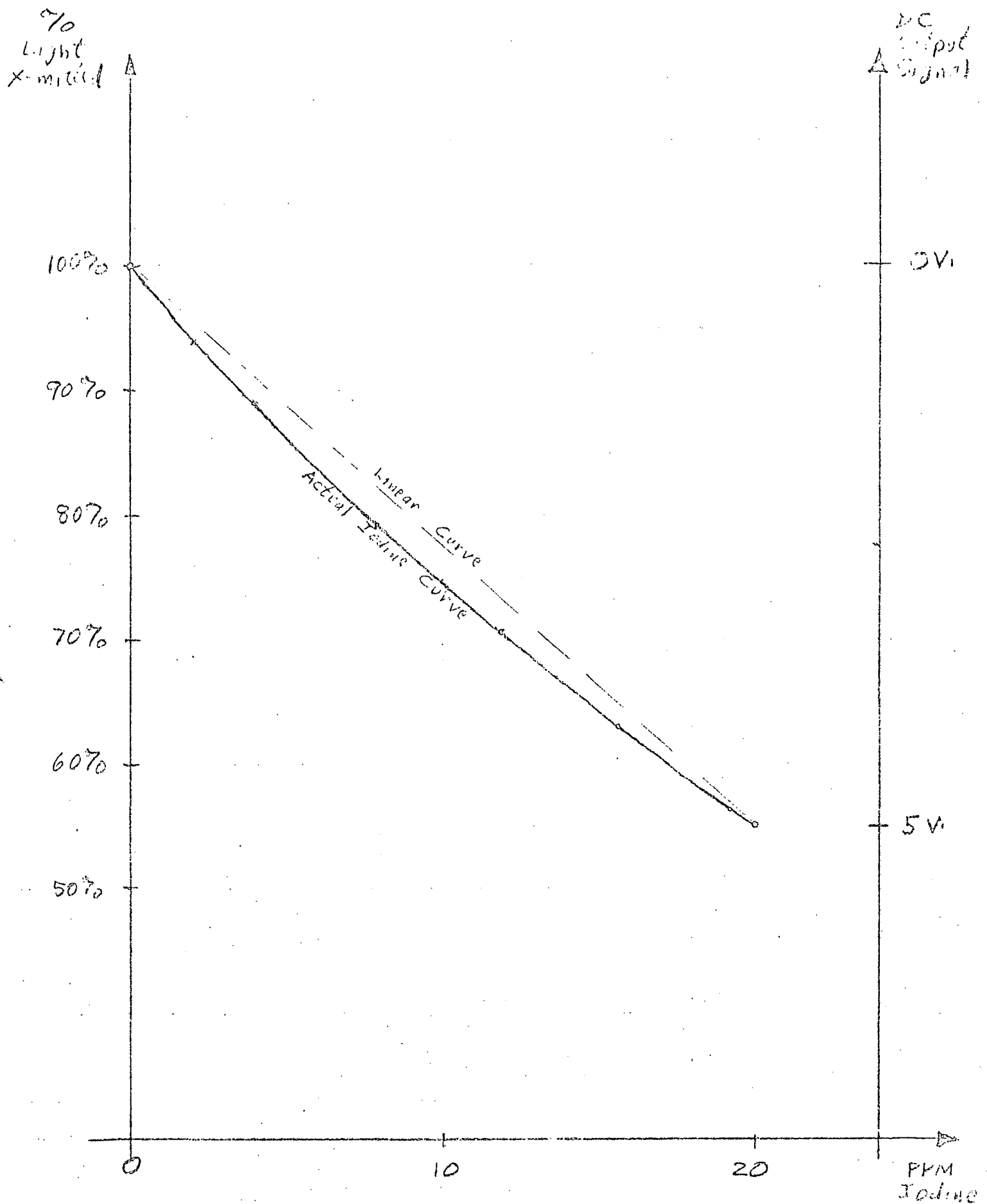
Figure 18. Non-Linearity Due to Iodine Solution

This gives rise to the curve in Figure 18. If it were carried beyond 20 ppm, it would asymptotically approach zero for an infinite concentration of iodine. This non-linear output (in contrast to a linear output shown as the idealized straight line) would make no difference in the operation and control of current iodine generator designs.

6.3   Timing and Power Control

It is assumed that the iodine monitor will turn on periodically, warm up for 10 minutes and then go through a brief sampling period. During this time a command signal (relay contact closure) and an analog signal (0 to 5 V representing 0 to 20 ppm of iodine) will be sent to the iodine generator. During the warm-up and sample intervals, the meter on the front panel of the monitor will display the iodine level. Water from the tank will normally be circulated through the iodine monitor, but during warmup and sample periods, the water flow will be shut off (to prevent noise input into the system).

In addition to the automatic operation of the monitor, a manual mode may also be used. The manual and automatic modes are separate and do not interfere with each other. If the operator places the manual mode switch to ON, a complete warmup cycle is initiated, but no signals are sent to the iodine generator. At the end of the 10 minute warmup period the unit shuts off automatically, or the operator may terminate the manual mode by placing the mode switch in OFF.

The base timer which generates the automatic sequence cycle will be a MOS counter Time-Base (Mostek MK5009P). This unit is essentially an oscillator which can have its frequency controlled by an external RC network, from one MHz down to dc. In addition, the unit may be programmed so that the output is the oscillator frequency divided by a factor ranging from unity up to 36×10^8. These counters can be set up to provide output pulse trains with periods in seconds, minutes, hours, or even years. The iodine monitor will be programmable for any desired sampling rate less than six times per hour.

When the base timer puts out a pulse at its programmed interval, it will activate two interval timers (which will also be Mostek MK5009P's). One interval timer will come on for ten minutes and the second one will come on for a slightly longer

time. Logic will look at the outputs of the two interval timers and control the meter, solenoid valve, relays, etc. When both interval timers are on, the monitor will be in the warmup phase. The measurement electronics will be activated, the solenoid valve will be shut off (through a transistor valve driver) and the panel meter will display the ppm of iodine. When one timer goes off, but the other is still on, the monitor is in the sample phase, which is identical to the warmup phase except that a relay closes and sends a command signal and analog signal out to the iodine generator. When both timers shut down, the monitor goes back to the standby phase, in which only the timer circuits have power. The solenoid valve opens again, and the measurement electronics is shut down.

When the operator places the monitor in the manual phase, a third interval timer (independent of the automatic timers) is turned on. This comes on for ten minutes, or until the operator terminates the manual phase. During this time, the monitor is placed in a mode identical to that of the warmup phase in automatic. The solenoid valve is closed, the measurement electronics comes on and ppm of iodine is displayed on the panel meter. After termination of the manual phase (by the operator or timer), the monitor goes back to the standby phase.

Power and signal switching will be done by small relays, except for the solenoid valve, which will be driven by a solid-state valve driver, capable of driving a load up to one ampere.

All dc voltages for the electronics will be obtained from a dc-dc converter, operating from the spacecraft power bus.

During standby, the monitor should dissipate between 360 and 367 milliwatts. During the warmup, sample and manual phases, the monitor will use much more power, which will largely depend on the type of solenoid valve used:

Component	Power (W)	
	Minimum Case	Maximum Case
Electronics	1.0	1.3
Motor	2.8	2.8
Lamp	18.0	20.0
Solenoid Valve	1.4	28.0
TOTAL	23.2	52.1

⊙ <u>Filter Wheel Motor and Driver</u>

The motor considered for this design is a stepping motor, but an alternate choice is a synchronous motor. In either case, an oscillator and a driver circuit would be required.

7.0   <u>CONCLUSIONS</u>

The feasibility of measuring iodine in iodine-iodide solutions over the specified range of 0-10 ppm by direct spectrophotometric techniques was established under a previous contract and verified by additional studies during the present endeavor. Turbidity and interfering chemical substances, at the maximum expected levels, do not introduce significant error in the free iodine determination. The Preliminary Design insures that the Iodine Monitor will operate in all orientations and be gravity independent. Manual operation of the system, except when desired, has been eliminated. The system is completely automated throughout, from sample introduction, instrument calibration and zeroing, to iodine readout. The present electronic design is quite flexible with respect to interfacing with an iodine generator. At this point, specific materials compatible with manned spacecraft requirements have not been called out for the preliminary design, but in view of the structures involved, we anticipate no problem in this area. Also, from the size and weight viewpoint, the present dimensions and mass could undoubtedly be minimized for a final design.

No expendables except electricity are required for this device, and the sample water is simply returned to the downstream system. No inflight maintenance is normally required, and the sample cell should not require cleaning during the longest mission. The spacecraft power of 28 Vdc will satisfy the voltage requirement of the Iodine Monitor.

8.0   RECOMMENDATIONS

Iodine spectroscopy shows four properties of iodine-iodide solutions which enhance the feasibility of an iodine colorimeter:

1. Iodine is sufficiently absorbent over the desired concentration range to be easily measured in a colorimeter system.

2. The free iodine component is measurable in the visible spectrum. This simplifies both optical and electrical systems.

3. The isosbestic point, required for accurate measurement, is located near the iodine maximum absorbance wavelength.

4. Scattering by particulate matter is nearly independent of wavelength. This means that the "adjustment" technique exercised at 650 nm (or 700 nm) is adequate for compensating turbidity effects.

Our Preliminary Design draws upon and exploits the experimental data which have clearly displayed the characteristics of these four properties. The next logical step, recommended here, is the translation of the Preliminary Design into a breadboard status for further study and refinement, to be followed by an automated prototype suitable for interfacing an iodine generator.